(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 364 271 B1**

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **18.01.95** (51) Int. Cl.[6]: **C09D 5/14**

(21) Application number: **89310477.8**

(22) Date of filing: **12.10.89**

The file contains technical information submitted after the application was filed and not included in this specification

(54) Antifouling coatings.

(30) Priority: **13.10.88 GB 8824003**
12.05.89 GB 8910970

(43) Date of publication of application:
18.04.90 Bulletin 90/16

(45) Publication of the grant of the patent:
18.01.95 Bulletin 95/03

(84) Designated Contracting States:
DE ES FR GB GR IT NL SE

(56) References cited:
EP-A- 0 201 279

DATABASE WPI, accession no. 76-65787x, Derwent Publications Ltd, London, GB; & JP-A-51 080 849

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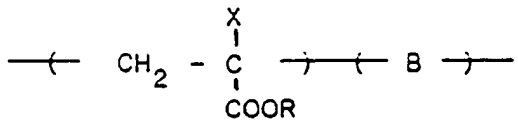
Description

This invention relates to antifouling coatings. antifouling coating is used as a top coat on ships' hulls to inhibit the settlement and growth of marine organisms such as barnacles and algae, generally by release of a biocide for the marine organisms.

Traditionally, antifouling coatings have comprised a relatively inert binder with a biocidal pigment which is leached from the paint. Among the binders which have been used are vinyl resins, particularly a vinyl chloride/vinyl acetate copolymer, and rosin. The vinyl resins are seawater-insoluble and paints based on them use a high pigment concentration so that there is contact between pigment particles to ensure leaching. Rosin is a hard brittle resin which is very slightly soluble in seawater. The biocidal pigment is very gradually leached out of the matrix of rosin binder in use, leaving a skeletal matrix of rosin which becomes washed off the hull surface to allow leaching of the biocidal pigment from deep within the paint film.

The most successful antifouling paints in recent years have been "self-polishing copolymer" paints based on a polymeric binder to which biocidal triorganotin moieties are chemically bound and from which the biocidal moieties are gradually hydrolysed by seawater, as described for example in GB-A-1457590. The polymer from which the triorganotin moieties have been hydrolysed becomes soluble in seawater, so that as the outermost paint layer becomes depleted of biocide it is swept off the surface of the hull by the movement of the ship through seawater. Self-polishing copolymer paints which release non-biocidal moieties are described in EP-B-69559 and EP-A-232006.

WO-A-84/02915 describes an anti-fouling paint having a hydrolysable film-forming water-insoluble seawater-erodible polymeric binder having recurring groups represented by the formula:



where X is hydrogen or methyl, R is an alkyl, aryl, aralkyl or triorganosilyl moiety and B is the residue of an ethylenically unsaturated comonomer. It has been found in practice that the less readily hydrolysable groups R such as benzyl, aminoalkyl or haloalkyl groups do not give a polymer which dissolves in seawater, whereas the more readily hydrolysable groups such as trialkylsilyl groups give a polymer which rapidly hydrolyses to a mechanically weak film in seawater.

JP-A-54-64633 describes a marine antifouling biocide which is a long-chain (12 to 18 carbon atoms) linear aliphatic primary amine or salt thereof. JP-A-54-110322 describes certain long-chain (12 to 18 carbon atoms) linear aliphatic secondary and tertiary amines as marine anti fouling agents.

US-A-4675051 describes a marine antifouling paint which is gradually dissolved in seawater and which comprises a binder which is a resin produced by the reaction of rosin and an aliphatic polyamine containing at least one primary or secondary amine group.

JP-51-80849A and its Derwent Abstract, 76-65787X, disclose that certain tricyclic diterpene amines are useful as bactericides, antibacterial agents, antifungal agents, detergents or resolving reagents.

The present invention seeks to provide antifouling compositions giving better results than those containing rosin alone as binder in the prevention of settlement and growth of barnacles and algae.

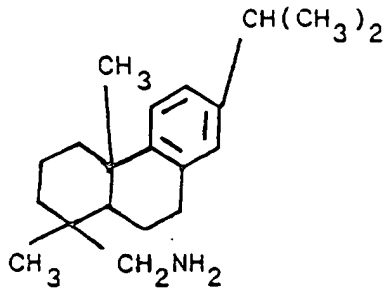
According to the present invention there is provided an antifouling coating composition comprising a film-forming binder and optionally a pigment, characterised in that the binder comprises 10-90% by weight of an amine of the formula:

(I)

where R^1 is a monovalent hydrocarbon group derived from a diterpene and R^2 and R^3 are each independently hydrogen, an alkyl group having 1-18 carbon atoms or an aryl group having 6-12 carbon atoms, and 10-90% by weight of rosin or a maleinised or fumarised rosin.

An amine of formula (I) acts both as a binder and as a marine antifouling biocide. The amine is preferably derived from rosin. The main constituent of rosin is abietic acid, which is mixed with other diterpene acids. The amine is preferably a primary or secondary amine. Secondary amines, for example

those in which R^2 is a methyl group, may be the more effective biocides against fouling by animals such as barnacles, whereas primary amines may be the more effective biocides against algae. A primary amine derived from rosin is dehydroabietylamine sold commercially as "Rosin Amine D". Its main constituent is



A corresponding secondary or tertiary amine, for example an N-methyl or N,N-dimethyl derivative of Rosin Amine D, can alternatively be used.

The amines of formula (I) are much more effective marine biocides than the amidoamines disclosed in US-A-4675051. The amines of formula (I) can be used in a clear antifouling varnish to be applied to ships' hulls and other marine surfaces. The amines can also be used in paint binders for paints containing pigments, which may or may not have antifouling activity. The amines described in the above-mentioned JP-A-54-64633 and JP-A-54-110322 are not suitable for use as binders for antifouling paints because they do not dry to a tack-free film when applied as a coating.

The binder of the antifouling coating compositions according to the invention is a mixture of an amine of formula (I) with rosin or a maleinised or fumarised rosin. The rosin or maleinised or fumarised rosin is slightly soluble or swellable in seawater. The binder contains 10 to 90%, preferably 35 to 80%, by weight of the amine and 90 to 10%, preferably 65 to 20%, by weight of the rosin or maleinised or fumarised rosin. The binder is erodible in use in seawater in the manner of known soluble matrix antifouling paints. The binder can be used as a clear antifouling varnish or with pigments, preferably a biocidal pigment such as cuprous oxide, to form an antifouling paint.

The binder can also contain a water-insoluble film-forming resin, for example a vinyl ether polymer such as a vinyl acetate/vinyl ether copolymer, for example that sold under the Trade Mark "Laroflex". The binder can also contain a less water-sensitive resin such as a vinyl chloride polymer, particularly a vinyl chloride/vinyl acetate copolymer, or a polyamide, particularly a polyamide formed from a dimer fatty acid such as those sold under the Trade Mark "Versamid". In this case it may be preferred to use a high pigment volume concentration of a pigment which is slightly soluble in or reactive with seawater such as cuprous oxide and/or zinc oxide. The amine can also be used with a non-toxic self-polishing binder polymer as described in US-A-4593055 or EP-A-232006, or with an organotin self-polishing copolymer as described in GB-A-1457590.

The binder can also contain one or more other high molecular weight amines as well as the amine of formula (I). The amine of formula (I) can for example be used with a long-chain (12 to 20 carbon atoms) aliphatic amine such as dodecyl amine, hexadecyl amine, octadecyl amine or oleyl amine, or a mixture of such amines, for example those sold as tallow amine, hydrogenated tallow amine, coconut amine, or N-methyl coconut amine. Although such long-chain amines are not suitable as paint binders or as varnishes when used alone, they may be useful in plasticising diterpene amines such as Rosin Amine D. Such a mixture of amines preferably contains at least 50% by weight of the amine of formula (I), for example 60 to 90%. Correspondingly, the long-chain aliphatic amine or the like is preferably present in an amount of from 5 to 50% by weight based on the weight of binder (including amine). One preferred form of antifouling paint binder or antifouling varnish according to the invention comprises a mixture of an amine of formula (I) with rosin and a long chain aliphatic amine, for example a mixture of 10-90% Rosin Amine D, 5-65% rosin and 5-50% of the aliphatic amine, by weight.

The antifouling paint binder can alternatively contain a high molecular weight, preferably polymeric, polyamine as well as the amine of formula (I). Such polyamines are available commercially as curing agents, particularly for epoxy resins. The "Versamid" polyamides derived from dimer fatty acids are often amino-functional. The polyamides sold under the Trade Mark "Casamid" are alternative amino-functional polyamides which are used as curing agents and are water-dispersible. These polyamines sold as curing agents are generally too sticky to be used alone as paint binders or varnishes. We have found that the

"Casamid" polyamines such as "Casamid 360" have marine biocidal properties, although these polyamines are less effective marine biocides than the amines of formula (I). The mixture of amines preferably contains at least 50%, more preferably 60 to 90%, by weight of the amine of formula (I).

The binder comprising an amine of formula (I) and rosin or maleinised or fumarised rosin can be mixed with a pigment using conventional paint blending procedures to provide a composition having a pigment volume concentration of, for example, 25 to 55%. The pigment is preferably a sparingly soluble pigment having a solubility in seawater of from 0.5 to 10 parts per million by weight, for example cuprous oxide, cuprous thiocyanate, zinc oxide, zinc ethylene bis(dithiocarbamate), zinc dimethyl dithiocarbamate, zinc diethyl dithiocarbamate or cuprous ethylene bis(dithiocarbamate). These sparingly soluble pigments which are copper and zinc compounds are generally marine biocides. These pigments produce water-soluble metal compounds on reaction with seawater so that the pigment particles do not survive at the paint surface. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithiocarbamate), which are highly effective biocidal pigments, can be mixed with zinc oxide, which is less effective as a biocide but dissolves slightly more rapidly in seawater. The binder comprising the amine of fomula (I) can be mixed with a basic pigment such as cuprous oxide or zinc oxide without gelation of the binder, unlike acid-functional polymers containing free carboxylic acid groups. The amine salt protects the acid groups against gelation by a basic pigment.

The paint composition can additionally or alternatively contain a pigment which is not reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 part per million by weight) such as titanium dioxide or ferric oxide or an organic pigment such as a phthalocyanine pigment. Such highly insoluble pigments are preferably used at less than 40% by weight of the total pigment component of the paint, most preferably less than 20%.

The antifouling paint can also contain a non-metalliferous biocide for marine organisms, for example tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, a substituted isothiazolone or 2-methyl-thio-4-t-butylamino-6-cyclopropylamino-s-triazine.

The antifouling coating of the invention is generally applied from a solution in an organic solvent, for example an aromatic hydrocarbon such as xylene or toluene, an aliphatic hydrocarbon such as white spirit, an ester such as butyl acetate, ethoxyethyl acetate or methoxypropyl acetate, an alcohol such as butanol or butoxy-ethanol or a ketone such as methyl isobutyl ketone or methyl isoamyl ketone.

Alternatively, the antifouling composition of the invention can be an aqueous composition containing water and a water-miscible cosolvent. Examples of cosolvents which can be used are alcohols such as butanol, glycol ethers such as methoxypropanol, methoxyethanol, butoxyethanol and ethoxyethanol and esters thereof such as methoxypropyl acetate. The amines of formula (I) are soluble in such mixtures of water and cosolvent but are substantially insoluble in water. Aqueous compositions whose binder contains an amine of formula (I) and a water-dilutable polyamine such as "Casamid 360" need only a low level of organic cosolvent, for example less than 200 g per litre.

The invention is illustrated by the following Examples.

Example 1

30% by volume Rosin Amine D and 20% by volume rosin were dissolved in 50% by volume "Shellsol" to form a clear antifouling varnish capable of gradually dissolving from a ship's hull on prolonged use in seawater.

The antifouling varnish of Example 1 was sprayed onto plaques, forming a clear coating film. The plaques were attached to a metal plate which was immersed in the sea at a site off the south coast of England rich in fouling organisms. The plaques were free of fouling after 12 months' immersion.

Example 2

A mixture of 80% by volume Rosin Amine D and 20% by volume rosin was dissolved in xylene and milled with a mixture of 93% by volume cuprous oxide and 7% by volume zinc oxide to give a paint of solids content 47% by volume and pigment volume concentration 47% (that is 47% by volume pigment in the dried paint film).

Example 3

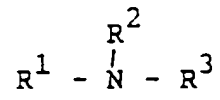
Example 2 was repeated using a mixture of 80% by volume rosin and 20% by volume Rosin Amine D.

The paints of Examples 2 and 3 were sprayed onto plaques and immersed in the sea as described above. They were still free of fouling after 12 months.

The paints of Examples 2 and 3 were also tested in a rotor test of the type described in GB-A-1457590. Both paints showed a gradual decrease in film thickness due to dissolution of the binder in seawater. The paint of Example 2 decreased in thickness at a rate half that of a successful commercial self-polishing copolymer antifouling paint. The paint of Example 3 decreased in thickness at a rate identical to that of the commercial paint.

Claims

1. An antifouling coating composition comprising a film-forming binder and optionally a pigment, characterized in that the binder comprises 10-90% by weight of an amine of the formula:



(I)

where R^1 is a monovalent hydrocarbon group derived from a diterpene and R^2 and R^3 are each independently hydrogen, an alkyl group having 1-18 carbon atoms or an aryl group having 6-12 carbon atoms, and 10-90% by weight of rosin or a maleinised or fumarised rosin.

2. An antifouling coating composition according to Claim 1, characterized in that the amine of formula (I) is a primary amine.

3. An antifouling coating composition according to Claim 2 characterized in that the amine of formula (I) is dehydroabietyl amine.

4. An antifouling coating composition according to any of Claims 1 to 3, characterized in that the binder comprises 10-80% by weight of the amine of formula (I) and 20-90% by weight rosin.

5. An antifouling coating composition according to Claim 4, characterized in that the binder comprises 35-80% by weight of the amine of formula (I) and 65-20% by weight rosin.

6. An antifouling coating composition according to any of Claims 1 to 5, characterised in that the composition additionally contains a polymeric polyamine.

7. An antifouling coating composition according to any of Claims 1 to 5, characterised in that the composition additionally contains up to 50% by weight, based on the total weight of binder (including amine), of an aliphatic amine having 12-20 carbon atoms.

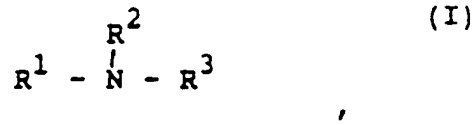
8. An antifouling coating composition according to Claim 1, characterised in that the composition contains 10-90% by weight dehydroabietylamine, 5-65% by weight rosin and 5-50% by weight of the aliphatic amine having 12-20 carbon atoms.

9. An antifouling coating composition according to any of Claims 1 to 8, characterised in that the coating is a substantially unpigmented clear varnish.

10. An antifouling coating composition according to any of Claims 1 to 8, characterised in that the composition contains a pigment which is sparingly soluble in sea water.

Patentansprüche

1. Antifouling-Überzugszusammensetzung enthaltend ein filmbildendes Bindemittel und gegebenenfalls ein Pigment, dadurch gekennzeichnet, daß das Bindemittel aus 10-90 Gew.-% eines Amins der Formel:



(I)

worin R^1 eine von einem Diterpen abgeleitete einwertige Kohlenwasserstoffgruppe und R^2 und R^3 jeweils unabhängig voneinander Wasserstoff, eine Alkylgruppe mit 1-18 Kohlenstoffatomen oder eine Arylgruppe mit 6-12 Kohlenstoffatomen bedeuten, und 10-90 Gew.-% Kolophonium oder mit Malein- oder Fumarsäure modifiziertes Kolophonium besteht.

2. Antifouling-Überzugszusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß es sich bei dem Amin der Formel (I) um ein primäres Amin handelt.

3. Antifouling-Überzugszusammensetzung nach Anspruch 2, dadurch gekennzeichnet, daß es sich bei dem Amin der Formel (I) um Dehydroabietylamin handelt.

4. Antifouling-Überzugszusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Bindemittel aus 10-80 Gew.-% des Amins der Formel (I) und 20-90 Gew.-% Kolophonium besteht.

5. Antifouling-Überzugszusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß das Bindemittel aus 35-80 Gew.-% des Amins der Formel (I) und 65-20 Gew.-% Kolophonium besteht.

6. Antifouling-Überzugszusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich ein polymeres Polyamin enthält.

7. Antifouling-Überzugszusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich bis 50 Gew.-%, bezogen auf das Gesamtgewicht an Bindemittel (einschließlich Amin), eines aliphatischen Amins mit 12-20 Kohlenstoffatomen enthält.

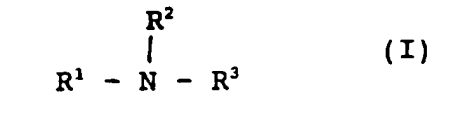
8. Antifouling-Überzugszusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung 10-90 Gew.-% Dehydroabietylamin, 5-65 Gew.-% Kolophonium sowie 5-50 Gew.-% des aliphatischen Amins mit 12-20 Kohlenstoffatomen enthält.

9. Antifouling-Überzugszusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der Überzug aus einem weitgehend nicht pigmentierten Klarlack besteht.

10. Antifouling-Überzugszusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Zusammensetzung ein in Meerwasser schwerlösliches Pigment enthält.

Revendications

1. Composition de revêtement anti-salissures, comprenant un liant filmogène et, éventuellement, un pigment, caractérisée en ce que le liant comprend 10-90% en poids d'une amine de formule:



(I)

dans laquelle R^1 est un groupe hydrocarboné monovalent dérivé d'un diterpène et R^2 et R^3 sont chacun indépendamment un atome d'hydrogène, un groupe alkyle comportant 1-18 atomes de carbone ou un groupe aryle comportant 6-12 atomes de carbone, et 10-90% en poids de colophane ou d'une colophane maléinisée ou fumarisée.

2. Composition de revêtement anti-salissures selon la revendication 1, caractérisée en ce que l'amine de formule (I) est une amine primaire.

3. Composition de revêtement anti-salissures selon la revendication 2, caractérisée en ce que l'amine de formule (I) est la déshydroabiétylamine.

4. Composition de revêtement anti-salissures selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le liant comprend 10-80% en poids de l'amine de formule (I) et 20-90% en poids de colophane.

5. Composition de revêtement anti-salissures selon la revendication 4, caractérisée en ce que le liant comprend 35-80% en poids de l'amine de formule (I) et 65-20% en poids de colophane.

6. Composition de revêtement anti-salissures selon l'une quelconque des revendications 1 à 5, caractérisée en ce que la composition contient en outre une polyamine polymère.

7. Composition de revêtement anti-salissures selon l'une quelconque des revendications 1 à 5, caractérisée en ce que la composition contient en outre jusqu'à 50% en poids, par rapport au poids total de liant (y compris l'amine), d'une amine aliphatique comportant 12-20 atomes de carbone.

8. Composition de revêtement anti-salissures selon la revendication 1, caractérisée en ce que la composition contient 10-90% en poids de déshydroabiétylamine, 5-65% en poids de colophane et 5-50% en poids de l'amine aliphatique comportant 12-20 atomes de carbone.

9. Composition de revêtement anti-salissures selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le revêtement est un vernis transparent essentiellement non pigmenté.

10. Composition de revêtement anti-salissures selon l'une quelconque des revendications 1 à 8, caractérisée en ce que la composition contient un pigment qui est peu soluble dans l'eau de mer.